

CLAIMS

1. Process facilitating the regeneration of a catalyst based on a zeolite, employed in an acylation reaction, characterized in that the zeolite is modified  
5 by addition of an effective quantity of at least one metallic element M chosen from the elements of group 8 of the Periodic Classification of the elements.

2. Process according to Claim 1, characterized in that the catalyst is a zeolite  
10 modified with the metallic element M chosen from iron, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum.

3. Process according to Claim 1, characterized in that the catalyst is a zeolite  
15 modified with the metallic element  $M_1$  chosen from ruthenium, rhodium, palladium, osmium, iridium and platinum.

4. Process according to either of Claims 2 and 3, characterized in that the catalyst is a zeolite  
20 modified with the metallic element M or  $M_1$  used in a quantity such that the percentage by weight of the metal relative to the zeolite is between 0.1 % and 25 %, preferably between 3 % and 15 %.

5. Process according to one of Claims 1 to 4, characterized in that the zeolite is a natural or synthetic zeolite.

6. Process according to Claim 5, characterized in that the zeolite is a natural zeolite

chosen from chabazite, clinoptilolite, erionite, mordenite, phillipsite and offretite.

7. Process according to Claim 5, characterized in that the zeolite is a synthetic zeolite chosen from:
- synthetic zeolites with a one-dimensional network such as zeolite ZSM-4, zeolite L, zeolite ZSM-12, zeolite ZSM-22, zeolite ZSM-23 and zeolite ZSM-48,
  - zeolites with a two-dimensional network, such as zeolite  $\beta$ , mordenite and ferrierite,
  - zeolites with a three-dimensional network such as zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZSM-11 and offretite.

8. Process according to Claim 7, characterized in that the zeolite is a zeolite  $\beta$  and Y.

9. Process according to Claims 1 to 8, characterized in that the metallic element(s) M or  $M_1$  are deposited on the zeolite especially by precipitation or by impregnation by a dry or wet route.

10. Process according to one of Claims 1 to 9, characterized in that the regeneration of the catalyst is conducted by sending a hot gaseous stream of molecular oxygen or of a gas containing it over the catalyst.

11. Process according to Claim 10, characterized in that pure oxygen or oxygen diluted with an inert gas, preferably air, is used.

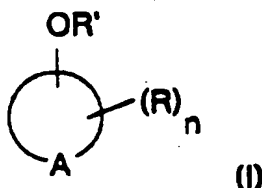
12. Process according to either of Claims 10

and 11, characterized in that the temperature of the gaseous stream is lower than 350°C and is preferably between 100°C and 250°C.

13. Process according to one of Claims 1 to 12, characterized in that a catalyst which can be reemployed in an acylation reaction is recovered.

14. Process for acylation of an aromatic ether, which consists in reacting an aromatic ether with an acylating agent, in the presence of a catalyst, and in then recovering the product formed, the said process being characterized in that the acylation reaction is conducted in the presence of an effective quantity of a zeolite modified with at least one element  $M_1$  of the platinum group.

15. Process according to Claim 14, characterized in that the aromatic ether corresponds to the general formula (I):



in which:

- A symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic aromatic carbocyclic system, the system including at least one OR' group, it being possible for the said cyclic residue to carry one or more substituents,

- R denotes one or a number of identical or different substituents,
  - R' denotes a hydrocarbon radical containing from 1 to 24 carbon atoms, which may be a linear or branched, saturated or unsaturated, acyclic aliphatic radical, a saturated or unsaturated cycloaliphatic or monocyclic or polycyclic aromatic radical, or a linear or branched, saturated or unsaturated, aliphatic radical carrying a cyclic substituent,
  - n is a number smaller than or equal to 4.
16. Process according to either of Claims 14 and 15, characterized in that the aromatic ether corresponds to the general formula (I) in which R' denotes:
- a linear or branched, saturated or unsaturated, acyclic aliphatic radical, preferably a linear or branched alkyl radical containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, it being possible for the hydrocarbon chain to be optionally interrupted by a heteroatom, a functional group and/or to carry a substituent,
  - a linear or branched, saturated or unsaturated, acyclic aliphatic radical carrying an optionally substituted cyclic substituent, it being possible for the said acyclic radical to be linked to the ring by a valency bond, a heteroatom or a functional group,
  - a carbocyclic radical which is saturated or includes 1 or 2 unsaturations in the ring, generally containing

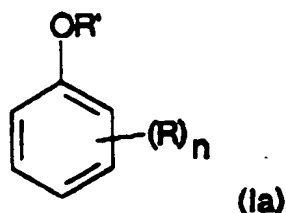
from 3 to 8 carbon atoms, preferably 6 carbon atoms in the ring, it being possible for the said ring to be substituted,

- a preferably monocyclic aromatic carbocyclic radical generally containing at least 4 carbon atoms, preferably 6 carbon atoms, in the ring, it being possible for the said ring to be substituted.

17. Process according to Claim 14, characterized in that the aromatic ether corresponds to the general formula (I) in which R' denotes a linear or branched alkyl radical containing from 1 to 4 carbon atoms, preferably a methyl radical or a phenyl radical.

18. Process according to one of Claims 14 to 17, characterized in that the aromatic ether corresponds to the general formula (I) in which the residue A denotes the residue of a monocyclic aromatic carbocyclic compound containing at least 4 carbon atoms and preferably 6 carbon atoms or the residue of a polycyclic carbocyclic compound, it being possible for the residue A to carry one or more substituents on the aromatic nucleus.

19. Process according to one of Claims 14 to 18, characterized in that the aromatic ether corresponds to the formula (Ia):



in which:

- n is a number smaller than or equal to 4, preferably equal to 0, 1 or 2,
- the radical R' denotes a linear or branched alkyl radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl or a phenyl radical,
- the radical(s) R denote one of the following atoms or groups:
  - a hydrogen atom,
  - a linear or branched alkyl radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl,
  - a linear or branched alkoxy radical containing from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy radicals,
  - a halogen atom, preferably a fluorine, chlorine or bromine atom, or a trifluoromethyl radical,
  - the radicals R' and R and the 2 successive atoms of the benzene ring can together form a ring containing from 5 to 7 atoms, optionally including another heteroatom.

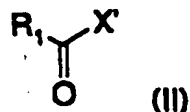
20. Process according to Claim 19,

characterized in that the aromatic ether corresponds to the formula (Ia) in which n is greater than or equal to 1, the radicals R' and R and the 2 successive atoms of the benzene ring may be linked together by an alkylene, alkenylene or alkenylidene radical containing from 2 to 4 carbon atoms to form a saturated, unsaturated or aromatic heterocyclic ring containing from 5 to 7 carbon atoms, in which one or more carbon atoms may be replaced by a heteroatom, preferably oxygen, the radicals R' and R preferably forming a methylenedioxy or ethylenedioxy radical.

21. Process according to either of Claims 19 and 20, characterized in that the aromatic ether corresponds to the formula (Ia) in which n is equal to 1, the radicals R and R' both denoting identical or different alkoxy radicals.

22. Process according to Claim 14 and 15, characterized in that the aromatic ether is anisole or veratrole.

23. Process according to one of Claims 14 to 22, characterized in that the acylating agent corresponds to the formula (II):



in which:

- R<sub>1</sub> denotes:

- a linear or branched, saturated or unsaturated,

aliphatic radical containing from 1 to 24 carbon atoms, a saturated, unsaturated cycloaliphatic or a monocyclic or polycyclic aromatic radical containing from 3 to 8 carbon atoms, or a linear or branched, saturated or unsaturated, aliphatic radical carrying a cyclic substituent,

- X' denotes:

- a halogen atom, preferably a chlorine or bromine atom,
- a hydroxyl group,
- a radical -O-CO-R<sub>2</sub> with R<sub>2</sub>, identical or different from R<sub>1</sub> having the same meaning as R<sub>1</sub>, it being possible for R<sub>1</sub> and R<sub>2</sub> to form together a linear or branched, saturated or unsaturated aliphatic divalent radical containing at least 2 carbon atoms.

24. Process according to Claim 23, characterized in that the acylating agent corresponds to the formula (II) in which X' denotes a chlorine atom and R<sub>1</sub> denotes a linear or branched alkyl radical containing from 1 to 12 carbon atoms, it being possible for the hydrocarbon chain to be optionally interrupted by a heteroatom or by a functional group or to carry a substituent, R<sub>1</sub> denotes an optionally substituted phenyl radical, or X' denotes a radical -O-CO-R<sub>2</sub> in which R<sub>1</sub> and R<sub>2</sub> are identical and denote an alkyl radical containing from 1 to 4 carbon atoms.



25. Process according to Claim 23 and 24, characterized in that the acylating agent is chosen from:

- acetic anhydride,
- 5 - propanoic anhydride,
- isobutyric anhydride,
- trifluoroacetic anhydride,
- benzoic anhydride,
- acetyl chloride,
- 10 - monochloroacetyl chloride,
- dichloroacetyl chloride,
- propanoyl chloride,
- isobutanoyl chloride,
- pivaloyl chloride,
- 15 - stearoyl chloride,
- crotonyl chloride,
- benzoyl chloride,
- chlorobenzoyl chlorides,
- p-nitrobenzoyl chloride,
- 20 - methoxybenzoyl chlorides,
- naphthoyl chlorides,
- acetic acid.

26. Process according to one of Claims 14 to 25, characterized in that the catalyst is a zeolite  
25 modified with the metallic element  $M_1$  chosen from ruthenium, rhodium, palladium, osmium, iridium and platinum.

27. Process according to one of Claims 14 to 26, characterized in that the catalyst is a zeolite modified with the metallic element  $M_1$  used in a quantity such that the percentage by weight of the metal  $M_1$  relative to the zeolite is between 0.1 % and 25 %, preferably between 3 % and 15 %.

28. Process according to one of Claims 14 to 27, characterized in that the zeolite is a natural or synthetic zeolite.

29. Process according to Claim 28, characterized in that the zeolite is a natural zeolite chosen from chabazite, clinoptilolite, erionite, mordenite, phillipsite and offretite.

30. Process according to Claim 28, characterized in that the zeolite is a synthetic zeolite chosen from:

- synthetic zeolites with a one-dimensional network such as zeolite ZSM-4, zeolite L, zeolite ZSM-12, zeolite ZSM-22, zeolite ZSM-23 and zeolite ZSM-48,
- zeolites with a two-dimensional network, such as zeolite  $\beta$ , mordenite and ferrierite,
- zeolites with a three-dimensional network such as zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZSM-11 and offretite.

31. Process according to Claim 29, characterized in that the zeolite is a zeolite  $\beta$  and Y.

32. Process according to one of Claims 14 to 31, characterized in that an organic solvent is used,

chosen from optionally halogenated, preferably  
chlorinated aliphatic and/or aromatic hydrocarbons,  
aliphatic, cycloaliphatic or aromatic ethers, nitro  
compounds, aliphatic or aromatic nitriles and  
5 tetramethylene sulphone.

33. Process according to one of Claims 14 to  
32, characterized in that the ratio of the number of  
moles of aromatic ether to the number of moles of  
acylating agent varies between 0.1 and 10 and  
10 preferably lies between 0.5 and 4.

34. Process according to one of Claims 14 to  
33, characterized in that in a noncontinuous method of  
operation the quantity of catalyst represents from 0.01  
to 50 %, preferably from 1.0 to 20 % by weight relative  
15 to the aromatic ether introduced and, in a continuous  
method of operation, the residence time of the flow of  
material on the catalyst bed varies between 5 min and  
10 hours and preferably between 15 min and 3 hours.

35. Process according to one of Claims 14 to  
20 34, characterized in that the temperature at which the  
acylation reaction is carried out lies between 20°C and  
300°C, preferably between 40°C and 200°C.

36. Process according to one of Claims 14 to  
35, characterized in that the regeneration of the  
25 catalyst is performed after removal of the liquid  
phase, according to the process described in one of  
Claims 10 to 12.

37. Process according to one of Claims 14 to 36, characterized in that a catalyst which can be reemployed in the acylation process of the invention as described in one of Claims 14 to 35 is recovered.

5           38. Catalyst for acylation of an aromatic ether, including a zeolite modified with an element of the platinum group.

          39. Catalyst for acylation of anisole,  
including a zeolite  $\beta$  modified with an element of the  
10   platinum group.